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(54) **LAMINATED BODY**

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a laminated body used for manufacturing a transfusion container, a food packaging or the like, wherein gas permeability is reduced and preservation properties of chemicals such as a transfusion or the like is improved, steam sterilization can be performed, and transparency, heat sealability and impact resistance are excellent.

SOLUTION: A laminated body is composed by forming an inorganic compound film on at least one side of a plastic film base and forming a coating layer having good adhesion properties to an adherent resin on the inorganic compound film, and laminating an adhering layer composed of the adherent resin and a protective film layer. And the laminated body has physical properties, wherein (1) an oxygen permeability before sterilization is 1cc/m2.24 hr.atm or lower; (2) a moisture permeability before sterilization is 1 g/m2.24 hr.atm or lower; (3) a light beam transmissivity is 55% or higher; and (4) a hue (b) value is 5 or lower.

TI Sterilizable laminates for chemical containers, infusion bags, and food packaging materials

IN Narita, Junichi; Komatsu, Hiroyuki; Suzuki, Akira; Iwamori, Akira

PA Mitsui Chemicals Inc., Japan

IC ICM B32B009-00
ICS B32B027-32; B65D065-40; C23C014-06

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PI JP 2000141535	A2	20000523	JP 1998-323808	19981113 <--
PRAI JP 1998-323808		19981113		

AB The laminates comprise plastic film substrates successively laminated with inorg. compound films, coating layer with high adhesion strength to the inorg. compds., adhesive polymer layers, and protective film layers to show O permeability ≤1 mL/m2-24 h-atm, moisture permeability ≤1 g/mm2-24 h-atm before sterilization, light transmittance ≥55%, and color b value ≤5%. Thus, Lumirror (PET film) was successively coated with Si **nitride oxide**, Al2O3, extrusion-laminated with an adhesive layer containing LDPE 15, linear polyethylene 15, ethylene-α-olefin copolymer 10, and maleated polyethylene 8%, and laminated with a polyethylene cast protective film to give a multilayer film with peeling strength 640 g/15-mm width, O and moisture permeabilities 0.1 mL/m2-24 h-atm and 1.0 g/m2-24 h-atm, resp., light transmittance 87%, and color b value 4.9%.

ST sterilizable plastic laminate silicon **nitride oxide** deposition; infusion bag transparent laminate film sterilizable; food packaging laminate plastic moisture oxygen impermeable; container chem sterilizable transparent laminate plastic

IT 1344-28-1, Alumina, uses 11105-01-4, Silicon **nitride oxide** 50926-11-9, ITO
RL: FFD (Food or feed use); PRP (Properties); TEM (Technical or engineered material use); THU (Therapeutic use); BIOL (Biological study); USES (Uses)
(sterilizable transparent laminates for chemical containers, infusion bags, and food packaging materials)

JP,2000-141535,A

CLAIMS

[Claim(s)]
[Claim 1] The layered product which the inorganic compound film is formed, a coating layer with a good adhesive property with adhesive resin is further formed on this inorganic compound film, and the laminating of the glue line and protection film layer which consist of adhesive resin is further carried out to at least one side of a plastic film base material, and is characterized by having the following physical properties.
(1) The oxygen transmittance before sterilization is 2-24 or less hr-atm of 1 cc/m.;
(2) The moisture vapor transmission before sterilization is 2-24 or less hr-atm of 1 g/m.;
(3) Light transmission is 55% or more.;
(4) A hue b value is five or less.;
[Claim 2] The layered product according to claim 1 characterized by the inorganic compound which forms said inorganic compound film being the amorphous acid silicon nitride whose sum of the concentration of four to oxygen density 64 atom %, three to nitrogen concentration 56 atom % and oxygen, and nitrogen is below 75 atom %.
[Claim 3] The layered product according to claim 1 characterized by said coating layer being a zinc oxide.
[Claim 4] The layered product according to claim 1 characterized by said coating layer being an aluminum oxide.
[Claim 5] The layered product according to claim 1 characterized by said coating layer being titanium oxide.
[Claim 6] The layered product according to claim 1 characterized by said coating layer being ITO (indium stannic-acid ghost).
[Claim 7] The layered product according to claim 1 characterized by being the polyolefine to which said adhesive resin denaturalized with unsaturated carboxylic acid or its derivative.
[Claim 8] The layered product according to claim 7 characterized by said polyolefine being an ethylene-alpha olefin random copolymer containing an ethylene homopolymer or other alpha olefins not more than 10 mol %.
[Claim 9] The layered product according to claim 7 characterized by said polyolefine being a propylene-alpha olefin random copolymer containing a propylene homopolymer or other alpha olefins not more than 10 mol %.
[Claim 10] The layered product according to claim 1 by which said protection film layer is using-ethylene system polymer, propylene system polymer, polyethylene terephthalate, polyamide, polycarbonate, and polyacrylonitrile characterized.
[Claim 11] The layered product according to claim 1 to 10 characterized by being an object for chemical containers. [Claim 12] The layered product according to claim 1 to 11 characterized by being an object for infusion solution containers.
[Claim 13] The layered product according to claim 1 to 10 characterized by being an object for food packing.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the layered product for food packing holding the layered product and the taste used as the ingredient of a chemical container and the infusion solution container which especially contains and saves infusion solutions, such as carbonic acid Ringer's solution and hydrolyzed vegetable protein.
[0002]
[Description of the Prior Art] Conventionally, as a chemical container, especially an infusion solution container, the glass thing has been used abundantly. However, by recent years, that it is easy to damage, since it is heavy, the use of the thing made from plastics of these has been increasing by the reasons of transportation cost increasing.
[0003] For this reason, gas cutoff nature especially oxygen cutoff nature, and steam cutoff nature of plastics had the case where the infusion solution shelf life of the infusion solution container made from plastics was inferior compared with a glass thing rather than it was necessarily enough. Therefore, although the technique of forming ceramic film, such as oxidation silicon and oxidation aluminum, was broadly performed by vacuum evaporationo, sputtering, CVD (chemical vapor deposition), etc. in order to barrier[high]-ize a packing material, sufficient gas barrier nature was not necessarily obtained.
[0004] this invention people have found out obtaining the film for chemical containers which has the gas barrier nature which was excellent in forming the amorphous acid silicon nitride film of a specific presentation at least in one side of plastic film compared with oxidization silicon or an aluminum oxide (Japanese Patent Application No. 10-088374).
[0005] Generally polyester, a polyamide, etc. are used from the ability of the outstanding gas barrier nature to be easily obtained as plastic film used as a base material. However, these films may need to laminate a heat-sealing layer, in order to use it as wrapping, since heat-sealing nature is not necessarily good. Moreover, a lamination may be performed in order to protect an inorganic compound layer.
[0006] There is a formula which obtains the multilayer film which has the protective layer of vacuum evaporationo or the spatter film by carrying out heating compression of both after applying the solution which distributed adhesives, such as an isocyanate system, a polyester system, a polyamide, and a polyimide system, to organic solvents, such as ethyl acetate, and making another film rival on the front face on the vacuum evaporationo formed on plastics one of the formulas of a lamination or the spatter film and which is called so-called dry lamination. However, with the above techniques, since an organic solvent remains into a film and shifts to contents liquid during use or preservation, it cannot use for the package gestalt which saves the drug solution with which the direct bodies, such as an infusion solution bag, are medicated. Moreover, there is a possibility of spoiling the taste of contents in food packing.
[0007] How to extrude and carry out a lamination as other lamination formulas on the inorganic compound layer formed on plastic film using the adhesive resin fused as a glue line can be considered. Resin is used for the glue line by this approach, and there is no component which shifts to contents liquid. However, it may exfoliate in the interface of adhesive resin and an acid silicon nitride film at the time of the wet sterilization processing usually performed for the infusion solution bag application etc. Therefore, in spite of having had the gas barrier nature excellent in the film in which the amorphous acid silicon nitride film was formed, it was not able to use as an infusion solution back package object.
[0008] Therefore, about the amino acid with which contents liquid deteriorates because oxygen invades, quality is held by wrapping the whole infusion solution bag package object in another high barrier package object. Moreover, the technique of carrying out dry lamination of the protective layer to vacuum evaporationo or the field which carried out the spatter is used for some the outside package objects in the silica or the aluminum

oxide. Under the present circumstances, although an organic solvent remains in the film of an outside package object, since space is between internal infusion solution bags, an organic solvent does not shift to the interior of an infusion solution bag. However, since invasion of the oxygen into an infusion solution bag starts after tearing an outside package object, there is also a possibility that it may use immediately after taking out from an outside package object at the time of use, and a pinhole may be vacant during preservation at an outside package object, and contents liquid may deteriorate, and high barrier-ization of the body of an infusion solution bag is desired.

[0009]

[Problem(s) to be Solved by the Invention] Wet sterilization processing is possible for it, and it offers the layered product used in order to create an infusion solution container, food packing, etc. excellent in transparency, heat-sealing nature, and shock resistance while this invention is made in view of the above-mentioned actual condition, reduces permeability and raises the shelf life of chemicals, such as an infusion solution.

[0010]

[Means for Solving the Problem] The inorganic compound film is formed, a coating layer with a good adhesive property with adhesive resin is further formed on this inorganic compound film, the laminating of the glue line and protection film layer which consist of adhesive resin is further carried out to at least one side of plastic film, and the layered product concerning this invention has the following physical properties.

(1) The oxygen transmittance before sterilization is 2-24 or less hr-atm of 1 cc/m.;

(2) The moisture vapor transmission before sterilization is 1 g/m2 and 24 hr-atm. Following;

(3) Light transmission is 55% or more.;

(4) A hue b value is five or less.;

[0011] Moreover, it is desirable that the above-mentioned inorganic compound is the amorphous acid silicon nitride whose sum of four to oxygen density 64 atom %, 3 - 56% of nitrogen concentration, and the concentration of oxygen and nitrogen is below 75 atom %. Moreover, as the above-mentioned coating layer, it is desirable to use a zinc oxide, an aluminum oxide, titanium oxide, or ITO (indium stannic-acid ghost). Moreover, it is desirable to use the polyolefine which denaturalized with unsaturated carboxylic acid or its derivative as adhesive resin. Moreover, as a protection film layer, it is desirable to use an ethylene system polymer and a propylene system polymer or polyethylene terephthalate, a polyamide, a polycarbonate, and a polyacrylonitrile. Hereafter, the layered product for infusion solution containers is explained to a detail also in the layered product concerning this invention, and the object for division chemical containers.

[0012] It is the film which consists of resin excellent in transparency, seal nature, and shock resistance as a plastics film base material used by <plastic film> this invention, for example, polyolefine film; polystyrene film; polyamide film; polycarbonate film; polyacrylonitrile films, such as polyester film; polyethylene, such as polyethylene terephthalate, polypropylene, and polybutene, etc. are mentioned.

[0013] Although an oriented film or an unstretched film is sufficient as the above-mentioned plastic film base material, in order to fill the light transmission of the layered product of this invention, the light transmission of a film base material needs to use at least 55% or more of thing. Moreover, in this invention, film thickness is desirable 0.01-1mm, and it is used.

[0014] Moreover, the best possible thing of the smooth nature on the above-mentioned front face of plastic film is desirable. When surface smooth nature is inferior, it is because there is a possibility that the gas barrier nature as a layered product concerning this invention may fall. As for surface smooth nature, it is desirable that Rmax (maximum of the difference of a crest and a trough, measured value of a surface roughness meter) showing surface roughness is 50nm or less, and it is desirable that it is 10 morenm or less.

[0015] Furthermore, in order to raise the adhesion over the above-mentioned

plastic film base material front face of the inorganic compound film mentioned later, well-known processing of the plasma treatment by inert gas, oxygen gas, etc. in defecation processing of washing for accepting the need, and degreasing and dehydrating on this base material front face etc. and a vacuum housing, such as helium, etc. may be performed.

[0016] As inorganic compound film of <inorganic compound film> this invention, an amorphous acid silicon nitride film is desirable. The amorphous acid silicon nitride film as used in the field of this invention is a vitrified thin film which contains oxygen and nitrogen and uses silicon as a principal component. The rate of the component element in the film can be continuously changed according to film formation conditions, and a membranous property changes in connection with it. In order to show the gas barrier nature which was excellent compared with film, such as oxidization silicon film and oxidization aluminum, it is desirable that it is the amorphous acid silicon nitride whose sum of the concentration of four to oxygen density 64 atom %, three to nitrogen concentration 56 atom % and oxygen, and nitrogen is below 75 atom %. The film of this elementary composition range shows high light transmission while it is excellent in the barrier nature of oxygen and a steam.

[0017] In order to form the acid silicon nitride film of a <generation method of amorphous acid silicon nitride film> amorphous substance, the material gas containing Si is used. As material gas containing Si and hydrogen, there are a silane, a disilane, etc., these are introduced with the gas and oxygen gas which contained nitrogen, such as ammonia and nitrogen gas, in the vacuum housing, the plasma is generated, and an amorphous acid silicon nitride film is formed on plastic film, for example. Moreover, as material gas containing Si, organosilicon compounds, such as a tetramethyl siloxane, hexa methyl disiloxane, and trimethylmethoxysilane, are also used. These are introduced into a vacuum housing as mixed gas with nitrogen gas and oxygen gas, generate the plasma, and form an acid silicon nitride film on plastic film.

[0018] How to understand by the plasma by the approach; electron cyclotron resonance understood by the plasma by the approach; microwave discharge which impresses the approach; RF which impresses a direct current and is understood by the plasma, for example as a means to excite the above-mentioned material gas introduced into the vacuum housing by the plasma, and is understood by the plasma; the approach of pyrolyzing with heating by the heat filament etc. is mentioned. In order to use plastic film as a base material in this invention, it is desirable to form membranes at low temperature, and the microwave CVD method which impresses the plasma-CVD method for impressing a direct current and a RF is desirable.

[0019] Moreover, physical vapor deposition, such as DC sputtering, RF sputtering, and ion beam sputtering, is employable as an approach of forming an amorphous acid silicon nitride film. In this case, the inorganic compound set by the film presentation as target material is used.

[0020] It is important for the thickness of an amorphous acid silicon nitride film that it is the range which does not spoil transparency, securing gas barrier nature, and in this invention, 10-300nm is desirable and is 20-100nm more preferably. Furthermore, if it is the same thickness, it is more desirable to divide and prepare an acid silicon nitride film in both sides in respect of gas barrier nature. For example, the direction which prepares the film with a thickness of 100nm in both sides shows [gas barrier nature] the inclination which becomes high rather than preparing the film with a thickness of 200nm in one side.

[0021] Carbon, a fluorine, or hydrogen can also be made to contain in order to improve the flexibility of the above-mentioned amorphous acid silicon nitride film. The presentation of an acid silicon nitride film can be analyzed using X-ray photoelectron spectroscopy, an X-ray micro analysis method and Auger electron spectroscopy, and a Rutherford backscattering method.

[0022] As a <coating layer> coating layer, from the point of an adhesive property with the base material resin of a glue line and safety, and health nature, it is desirable that they are a zinc oxide, an aluminum oxide, titanium oxide, and ITO (indium stannic-acid ghost), and a zinc oxide and an

aluminum oxide are desirable especially.
[0023] The above-mentioned coating layer is vacuum evaporationo or an approach like sputtering, and gives the above-mentioned inorganic compound on the inorganic compound film which was excellent in gas barrier nature. The above-mentioned coating layer may be formed by making it oxidize on the inorganic compound film, using metal zinc, metal aluminum, titanium metal, and an indium tin alloy as the source of vacuum evaporationo, or a sputtering target. Moreover, when it has conductivity like a zinc oxide and ITO (indium stannic-acid ghost), it can use as the source of vacuum evaporationo, or a sputtering target in the state of a compound. Moreover, a coating layer may be formed by RF sputtering, using an aluminum oxide and titanium oxide as a target.
[0024] As for the thickness of a coating layer, it is desirable from a point [need / homogeneity and to paste up with adhesive resin firmly / the vacuum evaporationo film] that it is 2nm - 100nm.
[0025] Even when the layered product of this invention is used for a chemical container, food packing, etc. by preparing this coating layer, the elevated temperature at the time of heat sterilization can be borne, and the layered product which does not start interfacial peeling between the inorganic compound film and a glue line can be obtained.
[0026] As <adhesive resin> adhesive property resin, the polyolefine which denaturalized with unsaturated carboxylic acid or its derivative is desirable. The propylene-alpha olefin random copolymer which contains the ethylene-alpha olefin random copolymer containing an ethylene homopolymer or ethylene, and other alpha olefins not more than 10 mol %, a propylene homopolymer or a propylene, and other alpha olefins not more than 10 mol % as polyolefine here is desirable.
[0027] moreover, as unsaturated carboxylic acid used for denaturation A maleic acid, an acrylic acid, boletic acid, a tetrahydrophtal acid, an itaconic acid, A citraconic acid, a crotonic acid, isocrotonic acid, the endo-cis bicyclo [2, 2, 1] hept-5-en -2, 3-dicarboxylic acid (trade name: NAJIKKU acid), etc. are desirable. Moreover, as the derivative, acid halide, an amide, imide, an anhydride, ester, etc. are mentioned, and, specifically, chlorination MARENIRU, maleimide, a maleic anhydride, an anhydrous citraconic acid, maleic-acid monomethyl, maleic-acid dimethyl, glycidil maleate, etc. are used. In these, unsaturated carboxylic acid or its anhydride is suitable, and a maleic acid, NAJIKKU acids, or these anhydrides are especially desirable. The thickness of this glue line is usually about 5-50 micrometers.
[0028] A <protection film layer> protection film layer is a layer of the film pasted up in order to protect vacuum evaporationo or the film which carried out the spatter on a base material. As a material, straight chain-like low density polyethylene, high pressure process low density polyethylene, Ethylene system polymers, such as medium density polyethylene and high density polyethylene, Although propylene system polymers, such as a propylene homopolymer, a propylene random copolymer, and a propylene block copolymer, polyethylene terephthalate, a polyamide, a polycarbonate, a polyacrylonitrile, etc. can be mentioned In these, it is desirable to use straight chain-like low density polyethylene, high pressure process low density polyethylene, medium density polyethylene, a propylene random copolymer, and a propylene block copolymer from the point of the rigidity of a product, transparency, and heat-sealing nature. An oriented film is sufficient as a film. The thickness of this protection film layer is usually about 10-100 micrometers.
[0029] Hereafter, this invention is explained, referring to a drawing. Drawing 1 is the sectional view of the layered product concerning this invention. For a plastic film base material and 2, as for a coating layer and 4, the inorganic compound film and 3 are [1 / a glue line and 5] protection film layers.
[0030] Moreover, drawing 2 is the mimetic diagram showing one example of the sputtering system used for formation of an amorphous acid silicon nitride film. drawing 2 -- setting -- 1 -- a vacuum housing and 2 -- a cooling roller and 3 -- a base material film and 4 -- glow discharge equipment and 5 -- target equipment and 6 -- winding -- taking out -- business -- as for a roll

and 7, the roll for rolling up and 8 are conveyance rolls.
[0031] After formation of the acid silicon nitride film by the sputtering method carries out oxygen glow processing of the base material film front face, it is performed by the approach of carrying out DC sputtering. As membrane formation actuation, first, let the inside of a vacuum housing be a high vacuum after installing a plastic film base material in the cooling roller 2 in a vacuum housing 1. The degree of vacuum at this time has desirable 0.2Pa or less, in order to lose the effect of impurity mixing into the film by the residual of other impurity gas. Next, oxygen is introduced so that it may become a predetermined pressure, a predetermined direct current is impressed, oxygen glow is generated, and a base material film front face is exposed into oxygen glow. As for the pressure of oxygen gas, at this time, it is [0.5-15Pa and a current] desirable that 0.2-0.5A, and an electrical potential difference are 500-2000V.
[0032] Next, an acid silicon nitride film is produced by DC sputtering. It introduces so that it may once become a predetermined pressure about argon gas and oxygen gas after exhaust air in a vacuum housing, and further, nitrogen generating gas, such as nitrogen gas and ammonia, is introduced so that it may become a predetermined pressure. The amounts of installation of oxygen and nitrogen generating gas differ "The oxygen of the acid silicon nitride film made into the purpose and nitrogen be comparatively alike." The pressure in the vacuum housing after introducing all gas is usually 0.2-10Pa.
[0033] Next, a predetermined direct current is impressed and the plasma of mixed gas is generated. As for a direct current, it is desirable that it is the range of Currents 5-20A and electrical potential differences 500-2000V. The plasma of mixed gas collides with the target which consists of metal silicon, and the silicon atom begun to beat by the impact of the plasma reacts with oxygen and nitrogen, it is deposited on a base material film front face, and an acid silicon nitride film is formed.
[0034] In order that the plasma-ized material gas atom may collide with a base material film, the temperature of a base material film rises. In order to make it the base material film 3 not deteriorate by this, it is desirable to hold the base material film 3 below to the glass transition point. This temperature control makes the cooling roller 2 which is the base material of the base material film 3 circulate through the liquid cooled by predetermined temperature, and is realized by controlling a cooling roller. As this liquid to circulate, the liquid cooled by predetermined temperature is mentioned, and as a liquid through which it circulates, water, ethylene glycol (antifreezing solution), alcohols, and when low-temperature-izing further, liquid nitrogen, liquid helium, etc. are used suitably. Although the method of circulating a gas is mentioned as other cooling approaches, the method of circulating a liquid from the point that heat capacity is large is desirable.
[0035] The oxygen transmittance before (1) sterilization the layered product of <layered product> this invention 1 cc/m2, 24 hr-atm or less, It is 2-24 or less hr-atm of 0.2 cc/m preferably, and the humidity before (2) sterilization is 5 g/m2 and 24 hr-atm. Following, They are 1 g/m2 and 24 hr-atm preferably. Since it is the following, gaseous permeability is low, and since film formation of the inorganic compound is carried out, and there is thermal resistance and it excels also in flexibility as a film further, it is suitable as an ingredient which creates the chemical container for conveying a liquid.
[0036] or [that it is still the same as a base material film on the formed inorganic compound film] -- or if the good transparency plastic film of different heat-sealing nature is laminated, since it can prevent that a membranous defect arises at the time of processing of heat sealing etc., it is desirable. As transparency plastic film which is excellent in heat-sealing nature, polyolefine system resin films, such as polyethylene and polypropylene, are illustrated. 5-1000 micrometers of 10-700 micrometers of thickness of the layered product after a lamination are 10-300 micrometers more preferably.
[0037] Moreover, for the layered product of this invention, (3) light transmission is 80% or more (4) hues preferably 55% or more. Since b value is three or less preferably five or less, while the oil level of the contents

liquid of an infusion solution container and discernment of a color are easy, even when contents change with mixing of a foreign matter etc. during preservation of a chemical, it can discover easily.

[0038] Furthermore, since the medicinal container obtained using the film of this invention has the above-mentioned physical properties, it is excellent in the mothball stability of infusion solutions which are easy to denaturalize, such as carbonic acid Ringer's solution and hydrolyzed vegetable protein. Moreover, since it is lightweight, it excels also in the transportability of contents.

[0039] The layered product of <manufacture approach of layered product> this invention is manufactured with an extrusion lamination process. An extrusion lamination process is the processing method for carrying out cooling solidification of the glue line with a cooling roller, and obtaining the film of a three-tiered structure, after extruding a thermoplastics melting film between continuation base materials, such as plastic film, and the film of another side and sticking by pressure and joining between the rubber covered roll for pressurization, and a cooling metal roll from a slit die.

[0040] Specifically, the layered product of this invention is manufactured by the following approaches. That is, the inorganic compound film is first prepared by the aforementioned approach on a plastic film base material, and a coating layer is further prepared by the aforementioned approach on it. A laminating is performed with an extrusion lamination process, using a glue line as an interlayer for such a plastic film base material and a protection film layer.

[0041]

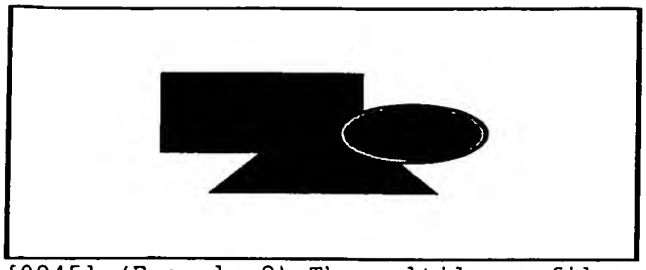
[Embodiment of the Invention] Hereafter, although the example of this invention is explained, this invention is not limited to these examples.

[0042]

[Example] (Example 1) It installed on the roll in the vacuum housing 1 which shows a polyethylene terephthalate film (trademark "lumiler" quantity transparence type) with a thickness of 25 micrometers to drawing 2 , and the inside of a vacuum housing was decompressed to 0.0133Pa. [by Toray Industries, Inc.] Oxygen gas was introduced into glow discharge equipment 4, the pressure was set as 1Pa, current 0.5A and a direct current of electrical-potential-difference 1000V were impressed, and glow processing was performed.

[0043] Subsequently, as material gas, the argon was introduced at a part for 82 cc/, nitrogen was set up and introduced at a part for 56 cc/, and the pressure of a reaction chamber was set to 0.3Pa. The direct current of 7A and 1000V was impressed using Si single crystal as a target. Membranes were formed rolling round a film the rate for 0.9m/. The thickness at this time was 48nm. 13 atom % Moreover, as a result of analyzing a membranous presentation using X-ray photoelectron spectroscopy, nitrogen and oxygen 44 atom % Reached, respectively, and were contained. As a result of measuring this base material film front face using an atomic force microscope (AFM), it is the maximum difference of elevation Rmax. It was 17nm (measuring range is 5micrometerx5micrometer).

[0044] The thin film vacuum evaporationo of the aluminum oxide was carried out by spatter processing at the high barrier film which carried out spatter processing of the acid silicon nitride film. Membranous thickness percentage is acid silicon nitride =12nm and aluminum-oxide =5nm. On maleic-acid conversion resin and a concrete target, the straight chain-like polyethylene of a consistency 0.920 on a vacuum evaporationo side Moreover, 52 % of the weight, The straight chain-like polyethylene of a consistency 0.965 15% of the weight for the high pressure process low-density-polyethylene resin of a consistency 0.920 15 % of the weight, The straight chain-like polyethylene of the consistency 0.965 which contains 10 % of the weight and a maleate for the ethylene-alpha olefine copolymer of a consistency 0.850 2.2% of the weight is blended at 8% of the weight of a rate. The multilayer film which film 50micrometer made from polyethylene which extruded, carried out lamination processing so that it might become the thickness of 20 micrometers as a glue line, and obtained beforehand the resin which carried out conversion within the extruder from cast molding was made to rival, and was made into the protective layer was obtained.



[0045] (Example 2) The multilayer film was manufactured by the same approach as an example 1 except having set the coating layer to aluminum-oxide =2.5nm.
[0046] (Example 3) The multilayer film was manufactured by the same approach as an example 1 except having set the coating layer to ITO(indium stannic-acid ghost) =2.5nm.
[0047]
[Comparative Example(s)] (Example 1 of a comparison) Except not preparing a coating layer, it is the same approach as an example 1, and the multilayer film was manufactured.
[0048] The following approach estimated the film of the <evaluation of layered product> above-mentioned example, and the example of a comparison.
(1) The gas permeability measuring device made from Mocon was used for moisture-vapor-transmission moisture vapor transmission, and it measured it on 40 degrees C and the conditions of 90% of relative humidity.
(2) Oxygen transmittance oxygen transmittance used the gas permeability measuring device made from YANAKO, and measured it under the 40-degree C oxygen ambient atmosphere.
(3) Whenever [light transmission and haze], and (HAZE) b value (yellow and blue comparatively)
Each value was measured using the integrating-sphere type hazemeter (ND[by Nippon Denshoku Co., Ltd.]-1001D). The wavelength of a measuring beam is 550nm.
(4) Peel strength was measured after performing wet sterilization processing for peel strength [of 115 degrees C] x 40 minutes. An exfoliation rate is a part for 50mm/.
[0049] The result of a trial is shown below.
[Table 1]

[0050]
[Effect of the Invention] Since wet sterilization processing is possible, the layered product concerning this invention can offer chemical containers, such as an infusion solution container excellent in mothball stability, while it is excellent in gas barrier nature. Furthermore, the above-mentioned layered product has high transparency, and since it is lightweight, it can offer the infusion solution container which became possible [discovering change of the contents by mixing of a foreign matter etc. easily], and was excellent in the transportability of a drug solution. Furthermore, it can use also as a food wrapping material using this property.
[0051]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the layered product for food packing holding the layered product and the taste used as the ingredient of a chemical container and the infusion solution container which especially contains and saves infusion solutions, such as carbonic acid Ringer's solution and hydrolyzed vegetable protein.

PRIOR ART

[Description of the Prior Art] Conventionally, as a chemical container, especially an infusion solution container, the glass thing has been used abundantly. However, by recent years, that it is easy to damage, since it is

heavy, the use of the thing made from plastics of these has been increasing by the reasons of transportation cost increasing.

[0003] For this reason, gas cutoff nature especially oxygen cutoff nature, and steam cutoff nature of plastics had the case where the infusion solution shelf life of the infusion solution container made from plastics was inferior compared with a glass thing rather than it was necessarily enough. Therefore, although the technique of forming ceramic film, such as oxidation silicon and oxidation aluminum, was broadly performed by vacuum evaporationo, sputtering, CVD (chemical vapor deposition), etc. in order to barrier[high]-ize a packing material, sufficient gas barrier nature was not necessarily obtained.

[0004] this invention people have found out obtaining the film for chemical containers which has the gas barrier nature which was excellent in forming the amorphous acid silicon nitride film of a specific presentation at least in one side of plastic film compared with oxidization silicon or an aluminum oxide (Japanese Patent Application No. 10-088374).

[0005] Generally polyester, a polyamide, etc. are used from the ability of the outstanding gas barrier nature to be easily obtained as plastic film used as a base material. However, these films may need to laminate a heat-sealing layer, in order to use it as wrapping, since heat-sealing nature is not necessarily good. Moreover, a lamination may be performed in order to protect an inorganic compound layer.

[0006] There is a formula which obtains the multilayer film which has the protective layer of vacuum evaporationo or the spatter film by carrying out heating compression of both after applying the solution which distributed adhesives, such as an isocyanate system, a polyester system, a polyamide, and a polyimide system, to organic solvents, such as ethyl acetate, and making another film rival on the front face on the vacuum evaporationo formed on plastics one of the formulas of a lamination or the spatter film and which is called so-called dry lamination. However, with the above techniques, since an organic solvent remains into a film and shifts to contents liquid during use or preservation, it cannot use for the package gestalt which saves the drug solution with which the direct bodies, such as an infusion solution bag, are medicated. Moreover, there is a possibility of spoiling the taste of contents in food packing.

[0007] How to extrude and carry out a lamination as other lamination formulas on the inorganic compound layer formed on plastic film using the adhesive resin fused as a glue line can be considered. Resin is used for the glue line by this approach, and there is no component which shifts to contents liquid. However, it may exfoliate in the interface of adhesive resin and an acid silicon nitride film at the time of the wet sterilization processing usually performed for the infusion solution bag application etc. Therefore, in spite of having had the gas barrier nature excellent in the film in which the amorphous acid silicon nitride film was formed, it was not able to use as an infusion solution back package object.

[0008] Therefore, about the amino acid with which contents liquid deteriorates because oxygen invades, quality is held by wrapping the whole infusion solution bag package object in another high barrier package object. Moreover, the technique of carrying out dry lamination of the protective layer to vacuum evaporationo or the field which carried out the spatter is used for some the outside package objects in the silica or the aluminum oxide. Under the present circumstances, although an organic solvent remains in the film of an outside package object, since space is between internal infusion solution bags, an organic solvent does not shift to the interior of an infusion solution bag. However, since invasion of the oxygen into an infusion solution bag starts after tearing an outside package object, there is also a possibility that it may use immediately after taking out from an outside package object at the time of use, and a pinhole may be vacant during preservation at an outside package object, and contents liquid may deteriorate, and high barrier-ization of the body of an infusion solution bag is desired.

EFFECT OF THE INVENTION

[Effect of the Invention] Since wet sterilization processing is possible, the layered product concerning this invention can offer chemical containers, such as an infusion solution container excellent in mothball stability, while it is excellent in gas barrier nature. Furthermore, the above-mentioned layered product has high transparency, and since it is lightweight, it can offer the infusion solution container which became possible [discovering change of the contents by mixing of a foreign matter etc. easily], and was excellent in the transportability of a drug solution. Furthermore, it can use also as a food wrapping material using this property.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Wet sterilization processing is possible for it, and it offers the layered product used in order to create an infusion solution container, food packing, etc. excellent in transparency, heat-sealing nature, and shock resistance while this invention is made in view of the above-mentioned actual condition, reduces permeability and raises the shelf life of chemicals, such as an infusion solution.

MEANS

[Means for Solving the Problem] The inorganic compound film is formed, a coating layer with a good adhesive property with adhesive resin is further formed on this inorganic compound film, the laminating of the glue line and protection film layer which consist of adhesive resin is further carried out to at least one side of plastic film, and the layered product concerning this invention has the following physical properties.
(1) The oxygen transmittance before sterilization is 2-24 or less hr-atm of 1 cc/m.;
(2) The moisture vapor transmission before sterilization is 1 g/m2 and 24 hr-atm. Following;
(3) Light transmission is 55% or more.;
(4) A hue b value is five or less.;
[0011] Moreover, it is desirable that the above-mentioned inorganic compound is the amorphous acid silicon nitride whose sum of four to oxygen density 64 atom %, 3 - 56% of nitrogen concentration, and the concentration of oxygen and nitrogen is below 75 atom %. Moreover, as the above-mentioned coating layer, it is desirable to use a zinc oxide, an aluminum oxide, titanium oxide, or ITO (indium stannic-acid ghost). Moreover, it is desirable to use the polyolefine which denaturalized with unsaturated carboxylic acid or its derivative as adhesive resin. Moreover, as a protection film layer, it is desirable to use an ethylene system polymer and a propylene system polymer or polyethylene terephthalate, a polyamide, a polycarbonate, and a polyacrylonitrile. Hereafter, the layered product for infusion solution containers is explained to a detail also in the layered product concerning this invention, and the object for division chemical containers.
[0012] It is the film which consists of resin excellent in transparency, seal nature, and shock resistance as a plastics film base material used by <plastic film> this invention, for example, polyolefine film; polystyrene film; polyamide film; polycarbonate film; polyacrylonitrile films, such as polyester film; polyethylene, such as polyethylene terephthalate, polypropylene, and polybutene, etc. are mentioned.
[0013] Although an oriented film or an unstretched film is sufficient as the above-mentioned plastic film base material, in order to fill the light transmission of the layered product of this invention, the light transmission of a film base material needs to use at least 55% or more of thing. Moreover, in this invention, film thickness is desirable 0.01-1mm, and it is used.
[0014] Moreover, the best possible thing of the smooth nature on the above-mentioned front face of plastic film is desirable. When surface smooth nature is inferior, it is because there is a possibility that the gas barrier nature as a layered product concerning this invention may fall. As for surface

smooth nature, it is desirable that Rmax (maximum of the difference of a crest and a trough, measured value of a surface roughness meter) showing surface roughness is 50nm or less, and it is desirable that it is 10 morenm or less.

[0015] Furthermore, in order to raise the adhesion over the above-mentioned plastic film base material front face of the inorganic compound film mentioned later, well-known processing of the plasma treatment by inert gas, oxygen gas, etc. in defecation processing of washing for accepting the need, and degreasing and dehydrating on this base material front face etc. and a vacuum housing, such as helium, etc. may be performed.

[0016] As inorganic compound film of <inorganic compound film> this invention, an amorphous acid silicon nitride film is desirable. The amorphous acid silicon nitride film as used in the field of this invention is a vitrified thin film which contains oxygen and nitrogen and uses silicon as a principal component. The rate of the component element in the film can be continuously changed according to film formation conditions, and a membranous property changes in connection with it. In order to show the gas barrier nature which was excellent compared with film, such as oxidization silicon film and oxidization aluminum, it is desirable that it is the amorphous acid silicon nitride whose sum of the concentration of four to oxygen density 64 atom %, three to nitrogen concentration 56 atom % and oxygen, and nitrogen is below 75 atom %. The film of this elementary composition range shows high light transmission while it is excellent in the barrier nature of oxygen and a steam.

[0017] In order to form the acid silicon nitride film of a <generation method of amorphous acid silicon nitride film> amorphous substance, the material gas containing Si is used. As material gas containing Si and hydrogen, there are a silane, a disilane, etc., these are introduced with the gas and oxygen gas which contained nitrogen, such as ammonia and nitrogen gas, in the vacuum housing, the plasma is generated, and an amorphous acid silicon nitride film is formed on plastic film, for example. Moreover, as material gas containing Si, organosilicon compounds, such as a tetramethyl siloxane, hexa methyl disiloxane, and trimethylmethoxysilane, are also used. These are introduced into a vacuum housing as mixed gas with nitrogen gas and oxygen gas, generate the plasma, and form an acid silicon nitride film on plastic film.

[0018] How to understand by the plasma by the approach; electron cyclotron resonance understood by the plasma by the approach; microwave discharge which impresses the approach; RF which impresses a direct current and is understood by the plasma, for example as a means to excite the above-mentioned material gas introduced into the vacuum housing by the plasma, and is understood by the plasma; the approach of pyrolyzing with heating by the heat filament etc. is mentioned. In order to use plastic film as a base material in this invention, it is desirable to form membranes at low temperature, and the microwave CVD method which impresses the plasma-CVD method for impressing a direct current and a RF is desirable.

[0019] Moreover, physical vapor deposition, such as DC sputtering, RF sputtering, and ion beam sputtering, is employable as an approach of forming an amorphous acid silicon nitride film. In this case, the inorganic compound set by the film presentation as target material is used.

[0020] It is important for the thickness of an amorphous acid silicon nitride film that it is the range which does not spoil transparency, securing gas barrier nature, and in this invention, 10-300nm is desirable and is 20-100nm more preferably. Furthermore, if it is the same thickness, it is more desirable to divide and prepare an acid silicon nitride film in both sides in respect of gas barrier nature. For example, the direction which prepares the film with a thickness of 100nm in both sides shows [gas barrier nature] the inclination which becomes high rather than preparing the film with a thickness of 200nm in one side.

[0021] Carbon, a fluorine, or hydrogen can also be made to contain in order to improve the flexibility of the above-mentioned amorphous acid silicon nitride film. The presentation of an acid silicon nitride film can be analyzed using X-ray photoelectron spectroscopy, an X-ray micro analysis method and Auger electron spectroscopy, and a Rutherford backscattering

method.
[0022] As a <coating layer> coating layer, from the point of an adhesive property with the base material resin of a glue line and safety, and health nature, it is desirable that they are a zinc oxide, an aluminum oxide, titanium oxide, and ITO (indium stannic-acid ghost), and a zinc oxide and an aluminum oxide are desirable especially.
[0023] The above-mentioned coating layer is vacuum evaporationo or an approach like sputtering, and gives the above-mentioned inorganic compound on the inorganic compound film which was excellent in gas barrier nature. The above-mentioned coating layer may be formed by making it oxidize on the inorganic compound film, using metal zinc, metal aluminum, titanium metal, and an indium tin alloy as the source of vacuum evaporationo, or a sputtering target. Moreover, when it has conductivity like a zinc oxide and ITO (indium stannic-acid ghost), it can use as the source of vacuum evaporationo, or a sputtering target in the state of a compound. Moreover, a coating layer may be formed by RF sputtering, using an aluminum oxide and titanium oxide as a target.
[0024] As for the thickness of a coating layer, it is desirable from a point [need / homogeneity and to paste up with adhesive resin firmly / the vacuum evaporationo film] that it is 2nm - 100nm.
[0025] Even when the layered product of this invention is used for a chemical container, food packing, etc. by preparing this coating layer, the elevated temperature at the time of heat sterilization can be borne, and the layered product which does not start interfacial peeling between the inorganic compound film and a glue line can be obtained.
[0026] As <adhesive resin> adhesive property resin, the polyolefine which denaturalized with unsaturated carboxylic acid or its derivative is desirable. The propylene-alpha olefin random copolymer which contains the ethylene-alpha olefin random copolymer containing an ethylene homopolymer or ethylene, and other alpha olefins not more than 10 mol %, a propylene homopolymer or a propylene, and other alpha olefins not more than 10 mol % as polyolefine here is desirable.
[0027] moreover, as unsaturated carboxylic acid used for denaturation A maleic acid, an acrylic acid, boletic acid, a tetrahydrophtal acid, an itaconic acid, A citraconic acid, a crotonic acid, isocrotonic acid, the endo-cis bicyclo [2, 2, 1] hept-5-en -2, 3-dicarboxylic acid (trade name: NAJIKKU acid), etc. are desirable. Moreover, as the derivative, acid halide, an amide, imide, an anhydride, ester, etc. are mentioned, and, specifically, chlorination MARENIRU, maleimide, a maleic anhydride, an anhydrous citraconic acid, maleic-acid monomethyl, maleic-acid dimethyl, glycidil maleate, etc. are used. In these, unsaturated carboxylic acid or its anhydride is suitable, and a maleic acid, NAJIKKU acids, or these anhydrides are especially desirable. The thickness of this glue line is usually about 5-50 micrometers.
[0028] A <protection film layer> protection film layer is a layer of the film pasted up in order to protect vacuum evaporationo or the film which carried out the spatter on a base material. As a material, straight chain-like low density polyethylene, high pressure process low density polyethylene, Ethylene system polymers, such as medium density polyethylene and high density polyethylene, Although propylene system polymers, such as a propylene homopolymer, a propylene random copolymer, and a propylene block copolymer, polyethylene terephthalate, a polyamide, a polycarbonate, a polyacrylonitrile, etc. can be mentioned In these, it is desirable to use straight chain-like low density polyethylene, high pressure process low density polyethylene, medium density polyethylene, a propylene random copolymer, and a propylene block copolymer from the point of the rigidity of a product, transparency, and heat-sealing nature. An oriented film is sufficient as a film. The thickness of this protection film layer is usually about 10-100 micrometers.
[0029] Hereafter, this invention is explained, referring to a drawing. Drawing 1 is the sectional view of the layered product concerning this invention. For a plastic film base material and 2, as for a coating layer and 4, the inorganic compound film and 3 are [1 / a glue line and 5] protection film layers.

[0030] Moreover, drawing 2 is the mimetic diagram showing one example of the sputtering system used for formation of an amorphous acid silicon nitride film. drawing 2 -- setting -- 1 -- a vacuum housing and 2 -- a cooling roller and 3 -- a base material film and 4 -- glow discharge equipment and 5 -- target equipment and 6 -- winding -- taking out -- business -- as for a roll and 7, the roll for rolling up and 8 are conveyance rolls.
[0031] After formation of the acid silicon nitride film by the sputtering method carries out oxygen glow processing of the base material film front face, it is performed by the approach of carrying out DC sputtering. As membrane formation actuation, first, let the inside of a vacuum housing be a high vacuum after installing a plastic film base material in the cooling roller 2 in a vacuum housing 1. The degree of vacuum at this time has desirable 0.2Pa or less, in order to lose the effect of impurity mixing into the film by the residual of other impurity gas. Next, oxygen is introduced so that it may become a predetermined pressure, a predetermined direct current is impressed, oxygen glow is generated, and a base material film front face is exposed into oxygen glow. As for the pressure of oxygen gas, at this time, it is [0.5-15Pa and a current] desirable that 0.2-0.5A, and an electrical potential difference are 500-2000V.
[0032] Next, an acid silicon nitride film is produced by DC sputtering. It introduces so that it may once become a predetermined pressure about argon gas and oxygen gas after exhaust air in a vacuum housing, and further, nitrogen generating gas, such as nitrogen gas and ammonia, is introduced so that it may become a predetermined pressure. The amounts of installation of oxygen and nitrogen generating gas differ "The oxygen of the acid silicon nitride film made into the purpose and nitrogen be comparatively alike." The pressure in the vacuum housing after introducing all gas is usually 0.2-10Pa.
[0033] Next, a predetermined direct current is impressed and the plasma of mixed gas is generated. As for a direct current, it is desirable that it is the range of Currents 5-20A and electrical potential differences 500-2000V. The plasma of mixed gas collides with the target which consists of metal silicon, and the silicon atom begun to beat by the impact of the plasma reacts with oxygen and nitrogen, it is deposited on a base material film front face, and an acid silicon nitride film is formed.
[0034] In order that the plasma-ized material gas atom may collide with a base material film, the temperature of a base material film rises. In order to make it the base material film 3 not deteriorate by this, it is desirable to hold the base material film 3 below to the glass transition point. This temperature control makes the cooling roller 2 which is the base material of the base material film 3 circulate through the liquid cooled by predetermined temperature, and is realized by controlling a cooling roller. As this liquid to circulate, the liquid cooled by predetermined temperature is mentioned, and as a liquid through which it circulates, water, ethylene glycol (antifreezing solution), alcohols, and when low-temperature-izing further, liquid nitrogen, liquid helium, etc. are used suitably. Although the method of circulating a gas is mentioned as other cooling approaches, the method of circulating a liquid from the point that heat capacity is large is desirable.
[0035] The oxygen transmittance before (1) sterilization the layered product of <layered product> this invention 1 cc/m2, 24 hr-atm or less, It is 2-24 or less hr-atm of 0.2 cc/m preferably, and the humidity before (2) sterilization is 5 g/m2 and 24 hr-atm. Following, They are 1 g/m2 and 24 hr-atm preferably. Since it is the following, gaseous permeability is low, and since film formation of the inorganic compound is carried out, and there is thermal resistance and it excels also in flexibility as a film further, it is suitable as an ingredient which creates the chemical container for conveying a liquid.
[0036] or [that it is still the same as a base material film on the formed inorganic compound film] -- or if the good transparency plastic film of different heat-sealing nature is laminated, since it can prevent that a membranous defect arises at the time of processing of heat sealing etc., it is desirable. As transparency plastic film which is excellent in heat-sealing nature, polyolefine system resin films, such as polyethylene and polypropylene, are illustrated. 5-1000 micrometers of 10-700 micrometers of

thickness of the layered product after a lamination are 10-300 micrometers more preferably.
[0037] Moreover, for the layered product of this invention, (3) light transmission is 80% or more (4) hues preferably 55% or more. Since b value is three or less preferably five or less, while the oil level of the contents liquid of an infusion solution container and discernment of a color are easy, even when contents change with mixing of a foreign matter etc. during preservation of a chemical, it can discover easily.
[0038] Furthermore, since the medicinal container obtained using the film of this invention has the above-mentioned physical properties, it is excellent in the mothball stability of infusion solutions which are easy to denaturalize, such as carbonic acid Ringer's solution and hydrolyzed vegetable protein. Moreover, since it is lightweight, it excels also in the transportability of contents.
[0039] The layered product of <manufacture approach of layered product> this invention is manufactured with an extrusion lamination process. An extrusion lamination process is the processing method for carrying out cooling solidification of the glue line with a cooling roller, and obtaining the film of a three-tiered structure, after extruding a thermoplastics melting film between continuation base materials, such as plastic film, and the film of another side and sticking by pressure and joining between the rubber covered roll for pressurization, and a cooling metal roll from a slit die.
[0040] Specifically, the layered product of this invention is manufactured by the following approaches. That is, the inorganic compound film is first prepared by the aforementioned approach on a plastic film base material, and a coating layer is further prepared by the aforementioned approach on it. A laminating is performed with an extrusion lamination process, using a glue line as an interlayer for such a plastic film base material and a protection film layer.
[0041]
[Embodiment of the Invention] Hereafter, although the example of this invention is explained, this invention is not limited to these examples.

EXAMPLE

[Example] (Example 1) It installed on the roll in the vacuum housing 1 which shows a polyethylene terephthalate film (trademark "lumiler" quantity transparence type) with a thickness of 25 micrometers to drawing 2 , and the inside of a vacuum housing was decompressed to 0.0133Pa. [by Toray Industries, Inc.] Oxygen gas was introduced into glow discharge equipment 4, the pressure was set as 1Pa, current 0.5A and a direct current of electrical-potential-difference 1000V were impressed, and glow processing was performed.
[0043] Subsequently, as material gas, the argon was introduced at a part for 82 cc/, nitrogen was set up and introduced at a part for 56 cc/, and the pressure of a reaction chamber was set to 0.3Pa. The direct current of 7A and 1000V was impressed using Si single crystal as a target. Membranes were formed rolling round a film the rate for 0.9m/. The thickness at this time was 48nm. 13 atom % Moreover, as a result of analyzing a membranous presentation using X-ray photoelectron spectroscopy, nitrogen and oxygen 44 atom % Reached, respectively, and were contained. As a result of measuring this base material film front face using an atomic force microscope (AFM), it is the maximum difference of elevation Rmax. It was 17nm (measuring range is 5micrometerx5micrometer).
[0044] The thin film vacuum evaporationo of the aluminum oxide was carried out by spatter processing at the high barrier film which carried out spatter processing of the acid silicon nitride film. Membranous thickness percentage is acid silicon nitride =12nm and aluminum-oxide =5nm. On maleic-acid conversion resin and a concrete target, the straight chain-like polyethylene of a consistency 0.920 on a vacuum evaporationo side Moreover, 52 % of the weight, The straight chain-like polyethylene of a consistency 0.965 15% of the weight for the high pressure process low-density-polyethylene resin of a consistency 0.920 15 % of the weight, The straight chain-like polyethylene of the consistency 0.965 which contains 10 % of the weight and a maleate for the

ethylene-alpha olefine copolymer of a consistency 0.850 2.2% of the weight is blended at 8% of the weight of a rate. The multilayer film which film 50micrometer made from polyethylene which extruded, carried out lamination processing so that it might become the thickness of 20 micrometers as a glue line, and obtained beforehand the resin which carried out conversion within the extruder from cast molding was made to rival, and was made into the protective layer was obtained.

[0045] (Example 2) The multilayer film was manufactured by the same approach as an example 1 except having set the coating layer to aluminum-oxide =2.5nm.

[0046] (Example 3) The multilayer film was manufactured by the same approach as an example 1 except having set the coating layer to ITO(indium stannic-acid ghost) =2.5nm.

[0047]

[Comparative Example(s)] (Example 1 of a comparison) Except not preparing a coating layer, it is the same approach as an example 1, and the multilayer film was manufactured.

[0048] The following approach estimated the film of the <evaluation of layered product> above-mentioned example, and the example of a comparison.

(1) The gas permeability measuring device made from Mocon was used for moisture-vapor-transmission moisture vapor transmission, and it measured it on 40 degrees C and the conditions of 90% of relative humidity.

(2) Oxygen transmittance oxygen transmittance used the gas permeability measuring device made from YANAKO, and measured it under the 40-degree C oxygen ambient atmosphere.

(3) Whenever [light transmission and haze], and (HAZE) b value (yellow and blue comparatively)

Each value was measured using the integrating-sphere type hazemeter (ND[by Nippon Denshoku Co., Ltd.]-1001D). The wavelength of a measuring beam is 550nm.

(4) Peel strength was measured after performing wet sterilization processing for peel strength [of 115 degrees C] x 40 minutes. An exfoliation rate is a part for 50mm/.

[0049] The result of a trial is shown below.

[Table 1]